SYNTHESIS of ORGANOSILICON MONOMERS

by

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Синтез кремнийорганических мономеров

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FOREWORD

The paradox of science as an international endeavor and science compartmentalized by numerous language barriers is one which chemists have faced for centuries. Time was when Latin stood as the universal language of chemistry, and communication was easier, at least within the small circle of the learned. Even then, we may suspect, there were difficulties with the reading of Arabic.

The literature of organosilicon chemistry is not free from the limitations of language, nor has it ever been. It is a lively subject, attracting workers from all of the classical divisions of chemistry and from all countries. Those who have been in it a long time have had to deal with a dozen languages, especially the Russian. I have among my valued papers copies of papers by Andrianov and Koton published in 1939, a Russian Patent issued in 1935 to Shtetter, and other papers of the same period by Ushakov and Itenberg, Volnov, and Reutt, and other researchers who published in the Russian journals. Some of these were kindly translated by E. H. Winslow; others I have struggled to understand myself, as I still do. I have had company in my difficulties; many other American workers have long agreed with me that our coverage of the Russian literature is insufficient. We are concerned about the brevity of abstracts, the expense and delays of translated journals, and (perhaps most important of all) the laboratory findings which never get into journal articles because they represent isolated items of experience and do not make a neat package for publication as a journal article.

Drs. Petrov, Miranov, Ponomarenko, and Chernyshev have now done us a great favor by writing a comprehensive account of their methods for synthesizing organosilicon substances, an account which includes a complete description of the compounds produced and their relationship to the previous classes of monomers. It is more than that: it is a guide to the literature and a survey of the present state of organosilicon chemistry, written from the point of view of the many active young groups working in Russia.

I am particularly happy that Consultants Bureau has chosen this admirable and significant volume to translate for the American reader; more than any other, it will give him a clear idea of the Russian views and practices in the synthesis of organosilicon compounds. It has no equivalent in English; it covers matters from a different point of view, and it concentrates especially on the synthesis and properties of unsaturated monomers and (in really comprehensive fashion, as Part Four) on the synthesis, conversion, and applications of organosilicon hydrides. The result is an invaluable addition to the American reference literature of chemistry for which we shall long be grateful.

Eugene G. Rochow
February 12, 1963

PREFACE

The chemistry of organosilicon compounds is an important field which provides industry with many special rubbers, liquids, lacquers, etc., and the rapid expansion of investigations in this field has made it imperative to generalize and systematize new data and review old theories. Several monographs on preparation methods and the use of silicones have appeared in the Soviet Union and abroad in recent years. The authors of these monographs attempted to cover as far as possible the whole range of problems associated with this field and therefore were unable to deal thoroughly with the separate sections of the organic chemistry of silicon. Nonetheless, a detailed examination of individual contemporary problems in this branch of science is also required.

The authors of the present monograph have been working for a long time on the synthesis of monomeric organosilicon compounds and the data that they have at their disposal are generalized in this book. It covers various synthetic methods and the properties of the most important, widely-used organosilicon monomers and is based on the work of the authors themselves and also literature data, including some work published in 1960.

The book may be of interest to scientists and postgraduate students working on organosilicon compounds and also to industrial engineers and students with appropriate specialties. In all sections of this monograph the physical properties of organosilicon compounds have been tabulated so that it may be used as a reference book.

The authors are very grateful to Corresponding Member of the Academy of Sciences of the USSR R. Kh. Freidlina and Candidate of Chemical Sciences M. G. Voronkov, who read the manuscript and made a number of valuable criticisms.

The Introduction and Chapters I, II, and IV, which are devoted to general problems in the chemistry of organosilicon compounds, were written by A. D. Petrov. Chapter III of Part 1 on the direct synthesis of organohalosilanes and Part 3 on methods of synthesizing aromatic and aliphatic–aromatic organosilicon monomers were written by E. A. Chernyshev. Chapter V of Part 1 on the effect of a silicon atom on the reactivity of carbofunctional organosilicon compounds was written by E. A. Chernyshev and V. F. Mironov; Part 2 on the synthesis and properties of unsaturated organosilicon compounds is by V. F. Mironov; and Part 4 on the synthesis and conversions of organic silicon hydrides is by V. A. Ponomarenko. A. D. Petrov, V. F. Mironov, and E. A. Chernyshev wrote the conclusion.

This arrangement of the material has forced us to examine some work briefly in the general section (Chapters I-V) and in more detail and from different points of view in the subsequent special sections. However, in arranging the material in this manner, we have tried to avoid repetition as far as possible without sacrificing clarity and thoroughness.

The present monograph is the first attempt by the authors to systematize the extensive material on the synthesis of organosilicon monomers and necessarily will leave some shortcomings. The authors will be grateful to readers for any critical comments they wish to offer.

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INTRODUCTION

The development of the chemistry of carbon and mainly of hydrocarbons and their derivatives was stimulated by the tremendous natural sources of hydrocarbons (petroleum) and many other organic substances (cellulose, fats, sugars, rubber, etc.).

The processing of these materials (production of coke, high-octane components of gasoline, synthetic aliphatic acids, and rubbers) in its turn led to new sources of a variety of hydrocarbon derivatives (coal tar components, alcohols, ketones, phenols, etc.).

The chemistry of the element closest to carbon in the Periodic System (silicon) is in a different state. Although the natural resources of silicon considerably exceed those of coal, oil, and all oxygen-containing hydrocarbon derivatives together, silicon is a constituent of natural inorganic high-polymer materials (silicates and sands) and great expenditure of energy is required to extract it from them in a free state. In contrast to hydrocarbons, silicohydrocarbons do not exist naturally. Moreover, there are no natural derivatives of silicon and carbon which also contain oxygen, nitrogen, or any other elements. In contrast to gaseous carbon dioxide, silicon dioxide is a high-polymer material, whose depolymerization requires the expenditure of a large amount of energy to separate the silicon from the oxygen and then to form chains of silicon and carbon (or silicon and oxygen), mainly through intermediate silicon halides.

It is not surprising, therefore, that until recently the practical value and industrial production of silicon compounds were limited to the so-called dimethylsilicones, obtained by Kipping's reaction:

$$(CH_3)_2SiCl_2 \xrightarrow[-2HCl]{2H_2O} (CH_3)_2Si(OH)_2 \longrightarrow [(CH_3)_2Si{-}O{-}]_n$$

This industry, which had very small beginnings, was started because of the need for heat- and frost-resistant materials and its development to production in tens of thousands of tons was the result of the change from the organomagnesium method of synthesizing dimethylsilyl chlorides and ethoxy derivatives of dimethylsilane:

$$Si(OC_2H_5)_4 + CH_3MgCl \longrightarrow (CH_3)_2Si(OC_2H_5)_2$$

to the so-called direct synthesis discovered by Rochow:

$$2CH_3Cl + Si/Cu \rightarrow (CH_3)_2SiCl_2$$

However, the direct synthesis, which is so convenient for the production of $(CH_3)_2SiCl_2$, is unsuitable for the production of mixed dichlorosilane derivatives (Cl_2SiRR') and also $C_{10}H_7SiCl_3$ and $CH_3(C_{10}H_7)SiCl_2$, etc.

The latter problems, which are important in the development of the production of heat-resistant silicon-containing monomers, has been solved successfully by the new pyrogenic syntheses (developed in the Institute of Organic Chemistry, Academy of Sciences USSR); the others may be solved by catalytic addition of hydrosilanes

$$CH_3HSiCl_2 + CH_2{=}CHCl \xrightarrow{600^\circ} (CH_2{=}CH)(CH_3)SiCl_2$$

$$HSiCl_3 + C_6H_5Cl \xrightarrow{600^\circ} C_6H_5SiCl_3 \qquad (50\% \text{ yield})$$

$$HSiCl_3 + \alpha\text{-}C_{10}H_7Cl \xrightarrow{600^\circ} \alpha\text{-}C_{10}H_7SiCl_3 \qquad (60\%\ \text{yield})$$

$$HSiCl_3 + CH{\equiv}CH \xrightarrow{H_2PtCl_6} CH_2{=}CH{-}SiCl_3$$

$$(CH_3)HSiCl_2 + CF_2{=}CF_2 \xrightarrow{H_2PtCl_6} CF_2HCF_2SiCl_2(CH_3) \quad \text{etc.}$$

The development of methods for synthesizing various aryl- and alkenylchlorosilanes is of great value.

In addition to the simplification of methods of preparing various siloxanes, the polymerization of alkenyl- and alkadienylsilanes is of undoubted practical interest.

Together with the polymerization of vinylsilanes, which proceeds under the action of peroxides by the same scheme as the polymerization of vinyl chloride or vinyl acetate:

$$n\,CH_2{=}CHSi{\leqslant} \rightarrow (-CH_2-\underset{\displaystyle Si{\leqslant}}{\underset{|}{CH}}-)_n$$

i.e., to form a polymer with silicon atoms in side chains, it is also possible to effect a polymerization to form a polymer containing silicon atoms in the main chain. This is achieved simply by the reaction of vinylhydrosilanes in the presence of H_2PtCl_6

$$n HSiR_2(CH{=}CH_2) \rightarrow \left(\begin{array}{c} R \\ | \\ -Si-CH_2-CH_2- \\ | \\ R \end{array} \right)_n$$

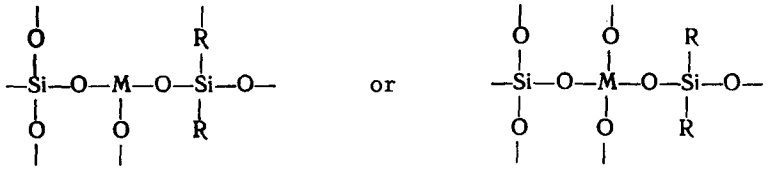
Polyorganosiloxanes are prepared under various conditions, depending on the polymer structure required. The synthesis of high-molecular solid polymers (rubbers) requires the monomer $(CH_3)_2SiCl_2$ in a highly pure state (99.97%) and the production of this involves considerable difficulties. Chemical purification methods are required in addition to accurate fractionation. Liquid polymers with the composition $R_3Si(-OSiR_2)-OSiR_3$ are synthesized by cohydrolysis of a mixture of R_3SiCl and R_2SiCl_2.

In addition to polyorganosiloxanes, organosiloxanocarbon polymers are synthesized. They are obtained either by cohydrolysis of α,ω-alkylene-bis-chlorosilanes and alkylchlorosilanes according to the scheme

$$Cl-\underset{\displaystyle R}{\underset{|}{Si}}-(CH_2)_n-\underset{\displaystyle R}{\underset{|}{Si}}-Cl + R_2SiCl_2 + H_2O \rightarrow$$

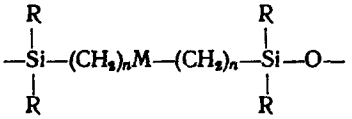
$$\rightarrow \left[\begin{array}{cccccc} R & & R & & R & \\ | & & | & & | & \\ -Si(CH_2)_n & Si & -O & Si & -O & - \\ | & & | & & | & \\ R & & R & & R & \end{array} \right]_x$$

or by hydrolysis of the first component alone. Finally, for the production of more and more heat-resistant materials, polyorganometallosiloxanes have been synthesized in recent years. Polyorganometallosiloxanes of type I



I

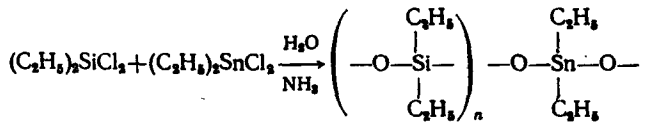
have already been obtained with M representing aluminum, titanium, tin, lead, antimony, etc. The next to be synthesized are polyorganometallosiloxanes of type II



II

i.e., compounds in which the metal is attached to carbon and not oxygen.

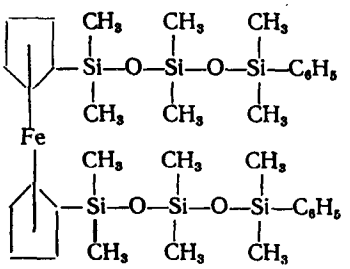
Polyorganometallosiloxanes of type I with. M = Sn have been obtained by co-hydrolysis of diethyldichlorotin and diethyldichlorosilane according to the scheme



The composition of the polyorganometallosiloxanes varies, depending on the ratio of monomers used for the reaction. (A polymer containing 56.8% of Sn and 13.4% of Si has been obtained.)

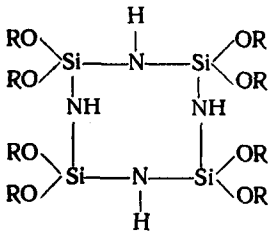
It was only a few years ago that there appeared the remarkable organometallic compound ferrocene, which is very readily synthesized from easily available materials. Nonetheless, we already have many derivatives of this compound, which is similar in properties to benzene; these include liquid, silicon-containing derivatives of ferrocene.

An example is compound III, which has a high heat-resistance and is used as a hydraulic fluid that remains liquid over the temperature range of -30 to +430°C.



III

Various polyorganometalloidosiloxanes with such metalloids as boron, nitrogen, and phosphorus have also been studied. An example is the tetrafunctional monomer with four NH groups and the composition $[Si(OR)_2]_4 \cdot (NH)_4$:



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The examples given already show that silicon is an excellent bridging atom for connecting either organic elements (C, H, and O) or inorganic elements (metals or metalloids) or both.

As we have pointed out above, the most important field of application of silicon is that of organosilicon and inorganosilicon (or semi-inorganosilicon) polymers, which have high heat- and frost-resistance.

This monograph consists of four parts.

The first two chapters of Part 1 are introductory and cover the similarities and differences between carbon compounds and structurally similar silicon compounds and also give a description of methods of synthesizing monomeric organosilicon compounds, namely, organometallic, catalytic, and pyrogenic methods.

Chapter III is devoted to the most important industrial method, namely the so-called direct synthesis of organic halosilanes, which form the basis of the whole synthesis of diverse organosilicon compounds.

Chapter IV, "Synthesis and Properties of Silicohydrocarbons," gives detailed data on this class of compounds, which is fundamental in organosilicon chemistry and occupies a similar position to hydrocarbons in organic chemistry.

Finally, in Chapter V we examine the reactivity of various functional groups in organosilicon compounds in α-, β-, and γ-positions relative to silicon. The characteristics of the reactions examined are explained by inductive and conjugation effects.

The special parts (Parts 2, 3, and 4) cover unsaturated and aromatic organosilicon compounds and also silicon hydrides, i.e., the main types of organosilicon monomers. We examine the synthesis and reactions of monomers in detail and hardly touch on the polymerization of monomers or the physical and technical properties of polymers as these problems form a special section of polymer chemistry.

Synthesis methods and properties of unsaturated organosilicon compounds are given in Part 2. A new general method of synthesizing alkenylsilanes, which is called high-temperature condensation or homolytic silylation, is examined. Particular classes of unsaturated compounds, namely, alkenoxysilanes and alkynylsilanes, are described in separate chapters. In the section on the polymerization of alkenylsilanes it is shown that these compounds may be used to obtain new polymeric materials.

Part 3 gives a description of one of the most important classes of organosilicon monomers, namely, aryl- and arylalkylhalosilanes. In this part of the monograph we examine the organometallic synthesis of arylhalosilanes and their halogenation, the silicoalkylation of aromatic compounds, and thermal and catalytic reactions of silicon hydrides with aromatic compounds in the liquid and gas phases. A separate section is devoted to a new method of synthesizing arylchlorosilanes, namely, the high-temperature gas-phase reaction of silicon hydrides with aryl halides.

The importance of silicon hydrides in the industrial synthesis of organosilicon monomers is demonstrated in Part 4. Supplementing direct synthesis, silicon hydrides with one, two, and three Si—H bonds make it possible to synthesize by simple methods halosilanes with various radicals and also diarylhalosilanes, which are obtained in low yields by direct synthesis.

In addition, with many examples it is shown that silicon hydrides can be used to synthesize diverse carbofunctional compounds which have been produced on ever-increasing scales in the last ten years.

Part One

INTRODUCTION TO THE CHEMISTRY OF ORGANOSILICON COMPOUNDS

Chapter I

SIMILAR AND DISSIMILAR FEATURES OF ORGANIC AND ORGANOSILICON COMPOUNDS

The specific characteristics of silicon, which occupies an intermediate position between a typical metalloid, carbon, and the metals of Group IV (Ge, Sn, and Pb), are responsible for the nature of the development of the chemistry of silicohydrocarbons and their derivatives, which differs from that of the chemistry of hydrocarbons.

Paraffin obtained in the Fischer–Tropsch process contains up to 120 carbon atoms, while in the Ziegler process for the polymerization of ethylene, 1000 and more carbon atoms are linked together in the normal chain of polyethylene obtained by this method. Silanes analogous to alkanes may be obtained with not more than 6 silicon atoms in the chain. However, when the hydrogen in silanes is replaced by chlorine, it is possible to construct longer chains containing up to 25 silicon atoms, while perchloroalkanes may exist only up to and including perchlorobutane. The replacement of the chlorine atoms by alkyl or aryl radicals, i.e., the change to organosilicon compounds strengthens the bond between the silicon atoms in the main chain even more. By treating $(C_6H_5)_2SiCl_2$ or $(CH_3)_2SiCl_2$ with sodium, Kipping [1] and later Burkhard [2] obtained compounds of the type $(R_2Si-)_n$, in which n varies from 8 to 55. Compounds of even higher molecular weight may be obtained when silicon and oxygen atoms alternate in the main chain.

Like some other elements of the second period, silicon is unable to give stable double or triple bonds either with other silicon atoms or with carbon and this naturally reduces the possibilities of synthesizing high-polymer materials from organosilicon compounds. However, a compensation for this disadvantage is the capacity of dialkyl(diaryl)dichlorosilanes, unlike dialkylchloromethanes, for polymerization or, more accurately, polycondensation during hydrolysis according to the scheme

$$nR_2Si(OH)_2 \rightarrow (R_2SiO-)_n$$

Unlike carbon, which has both a valence and a coordination number of 4, silicon has a valence of 4 and a coordination number of 6. This also has a certain effect on the behavior of organosilicon compounds and, in particular, makes the bonds of silicon with other elements more labile than the bonds of carbon with the same elements. The difference in the behavior of silicon and carbon compounds also depends on the high atomic volume and large electron shell of silicon in comparison with those of carbon.

The electronegativity of silicon is considerably lower than that of carbon and approaches the electronegativities of Group IV metals (Pb—1.5; Sn—1.7; Ge—1.7; Si—1.8; C—2.5). As a result of this, the energies of bonds of silicon with elements with a high electronegativity (oxygen and halogens) are higher than those of bonds of carbon with the same elements (Si—O 160 kcal/mole; C—O 30.9 kcal/mole; Si—Cl 90.3 kcal/mole; C—Cl 77.9 kcal/mole; Si—F 134 kcal/mole; C—F 102 kcal/mole).

The lower electronegativity of the silicon atom and the higher polarizability of its electron shell make a silicon—halogen bond more ionizable than a carbon—halogen bond and this is responsible for the high reactivity of silicon—halogen bonds in many reactions. On the other hand, the energies of bonds of silicon with

elements with a low electronegativity are lower than those of bonds of carbon with the same elements. Thus, for example, the energy of the Si—H bond is approximately 80 kcal/mole, while that of the C—H bond is approximately 98 kcal/mole and the hydrogen is negative relative to the silicon atom in the case of Si—H, while it is positive in C—H. The energy of the C—C bond (approximately 85 kcal/mole) is higher than that of the Si—C bond (approximately 75 kcal/mole) and this is also responsible for the high lability of the latter, especially in heterolytic (ionic) cleavage.

Moreover, it should be noted particularly that the energy of the Si—C bond falls quite rapidly with an increase in the length of the radical. Thus, the energy of the Si—CH_3 bond is 74 kcal/mole, Si—C_2H_5 62 kcal/mole, Si—C_3H_7 69 kcal/mole, and Si—C_4H_9 54 kcal/mole [3].

The Si—X bond is of particularly great importance in the chemistry of organosilicon compounds as almost all organosilicon compounds are ultimately obtained from elementary silicon through $SiCl_4$ and alkyl(aryl)halosilanes. The Si—X bond is much more reactive than the C—X bond toward polar reagents. The ease of hydrolysis of halosilanes decreases with the successive replacement of halogens by alkyls or aryls. There is the reverse relation with analogous carbon compounds. The Si—H bond is much more reactive than the C—H bond. A hydrogen halide reacts with this bond in the presence of AlX_3 to form halosilanes and hydrogen. The polarizability of the Si—H bond is similar to C—Cl rather than C—H and therefore, many reactions of hydrosilanes are similar to the reactions of alkyl halides. For example, the reaction

$$R_3SiH + HOR' \xrightarrow{NaOR'} R_3SiOR' + H_2$$

is similar to the Williamson synthesis of ethers from alkyl halides and not the reaction of an analog with a tertiary carbon. Hydrosilanes add readily to double and triple bonds of various organic compounds in the presence of catalysts and this will be discussed in detail below. Hydrosilanes condense with alkenyl halides at high temperatures in the absence of catalysts according to the scheme

$$\gtrless SiH + RCl \rightarrow HCl + \gtrless SiR$$

i.e., to form HCl and alkenylsilanes.

The reactivity of the bond $\gtrless$Si—H decreases as the hydrogens at the silicon atom are replaced by alkyls or aryls. While SiH_4 reacts vigorously with bromine even at low temperatures, the bromination of $(C_6H_5)_3Si$—H proceeds slowly even in boiling CCl_4. This is all contrary to well-known facts on the reactivity of secondary and tertiary C—H bonds. Thus, while the reactivity changes in the following order in hydrocarbon compounds: $CH_3 < CH_2 < CH$, it changes in the reverse order in hydrosilicon compounds: $SiH_3 > SiH_2 > SiH$. However, even in a trialkylsilane R_3Si—H, the Si—H bond is still much more reactive than the C—H bond in structurally similar compounds. This is indicated by the following reactions [4-6]:

$$R_3SiH + R'COCl \rightarrow R_3SiCl$$

$$R_3SiH + NH_2R' \rightarrow R_3SiNHR'$$

$$R_3SiH + HCOOR' \rightarrow R_3Si{-}O{-}\overset{\overset{O}{\|}}{C}{-}R'$$

which do not occur with tertiary hydrocarbons.

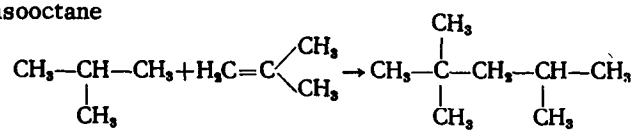
Triphenylsilane and triethylsilane react with organolithium compounds to form tetrasubstituted silanes [7]:

$$R_3SiH + R'Li \rightarrow R_3SiR' + LiH$$

while triphenylmethane reacts in the reverse order [8]:

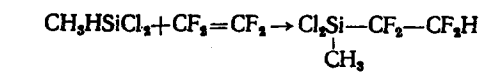
$$R_3CH + R'Li \rightarrow R_3CLi + R'H$$

It should also be noted that tertiary hydrocarbons condense with olefins with difficulty under the action of strong reagents (H_2SO_4 and $AlCl_3$); for example, in the synthesis of isooctane

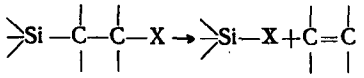


The reaction of the silicon analogs of tertiary hydrocarbons with unsaturated hydrocarbons and even their halogen derivatives proceeds much more readily (in the presence of platinum on a carrier) [9, 10]

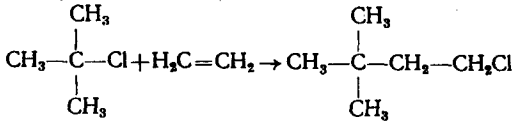
$$(C_2H_5)_3SiH + CH \equiv CH \rightarrow (C_2H_5)_3Si-CH=CH_2$$



The effect of silicon is not limited to bonds by which it is directly attached to carbon or other elements, but extends to more remote bonds, even in the absence of conjugated double bonds. A large number of investigations in this field have been carried out by Whitmore, who originated the term "Si effect." He was the first to synthesize siliconeopentyl chloride $(CH_3)_3SiCH_2Cl$ and showed that the halogen here is more reactive toward nucleophilic reagents [11] than in neopentyl chloride. He explained the higher reactivity by lower steric hindrance. However, siliconeopentyl chloride was found to be less reactive toward $AgNO_3$ than the corresponding alkyl halide. This is explained by the high electronegativity of the radical in siliconeopentyl chloride, which hampers electrophilic attack on the halogen. Another interesting phenomenon is the so-called β-effect, i.e., the tendency of compounds with a halogen at a β-carbon to decompose under the action of heat and Grignard reagents:



The degree of this decomposition depends both on the nature of the radicals R at the silicon atom and on the nature of the attacking reagent RMgX [12]. The decomposition depends on the presence of the two polarized bonds C—X and Si—C in a conjugated position. Silicon compounds differ from carbon compounds in β-decomposition as with the latter there is the reverse reaction in the synthesis of the structural analog of the β-halide by condensation of tertiary butyl chloride (or its analogs) with ethylene



At the same time, β-decomposition demonstrates the relation between silicon compounds and analogous organometallic compounds which undergo similar decomposition under the action of Grignard reagents:

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